
NATO ARW, Kyiv, Sept. 07–13 2003

The Main Tendencies in Elaboration of Materials with High Specific Strength



Professor S. Firstov

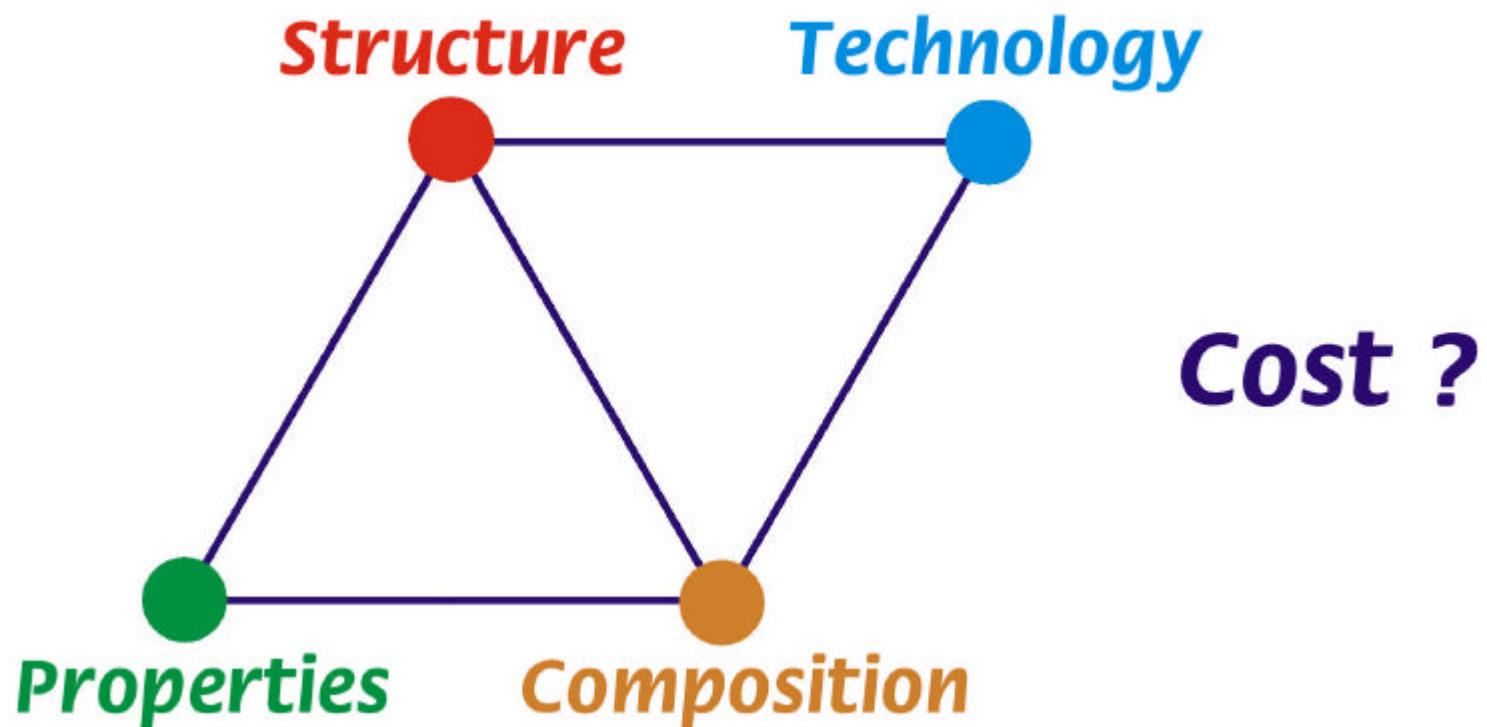


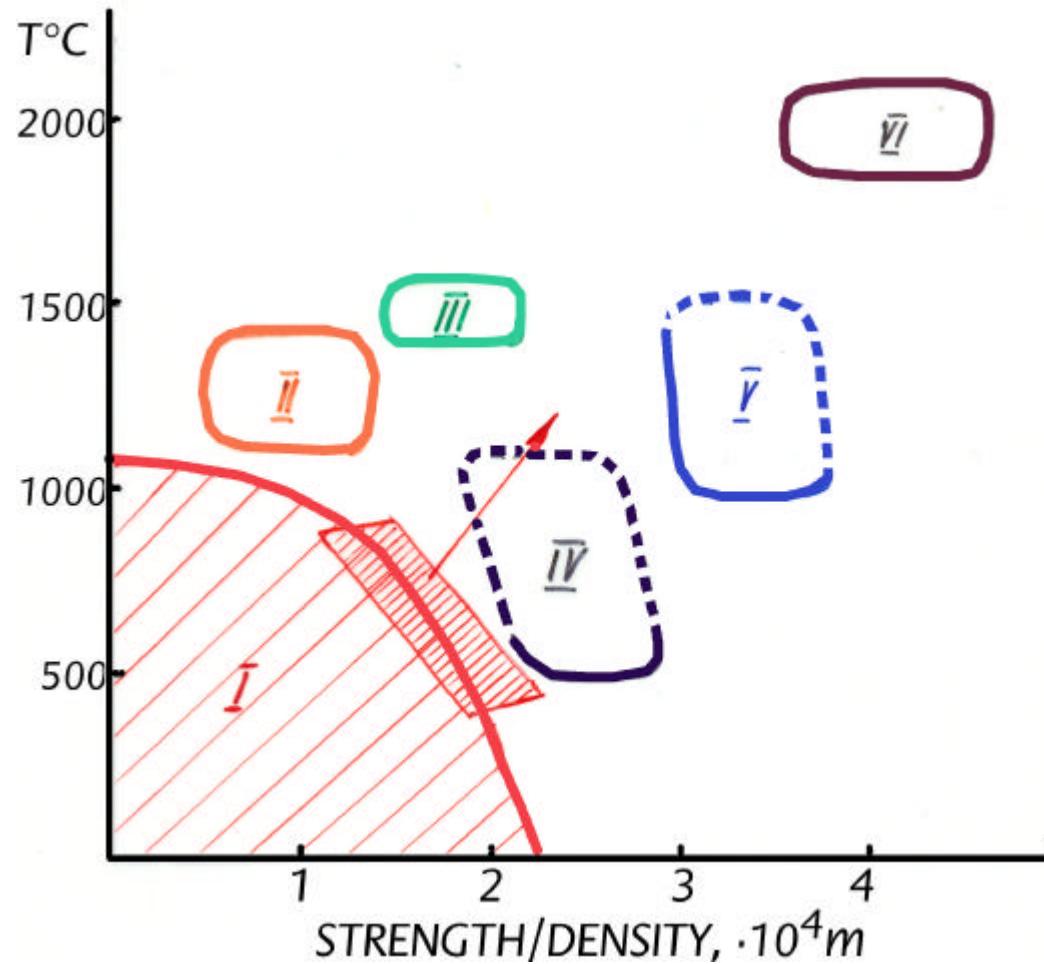
I.M. Frantcevych Institute for Problems of Materials Sciences

Kyiv, Ukraine

Report Documentation Page			Form Approved OMB No. 0704-0188	
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- Introduction
- Nanostructured materials
- Ti-Si-X and Ti -B-X systems as the base for elaboration of new in situ composites
- Conclusions





I - Conventional materials,
Ti and superalloys

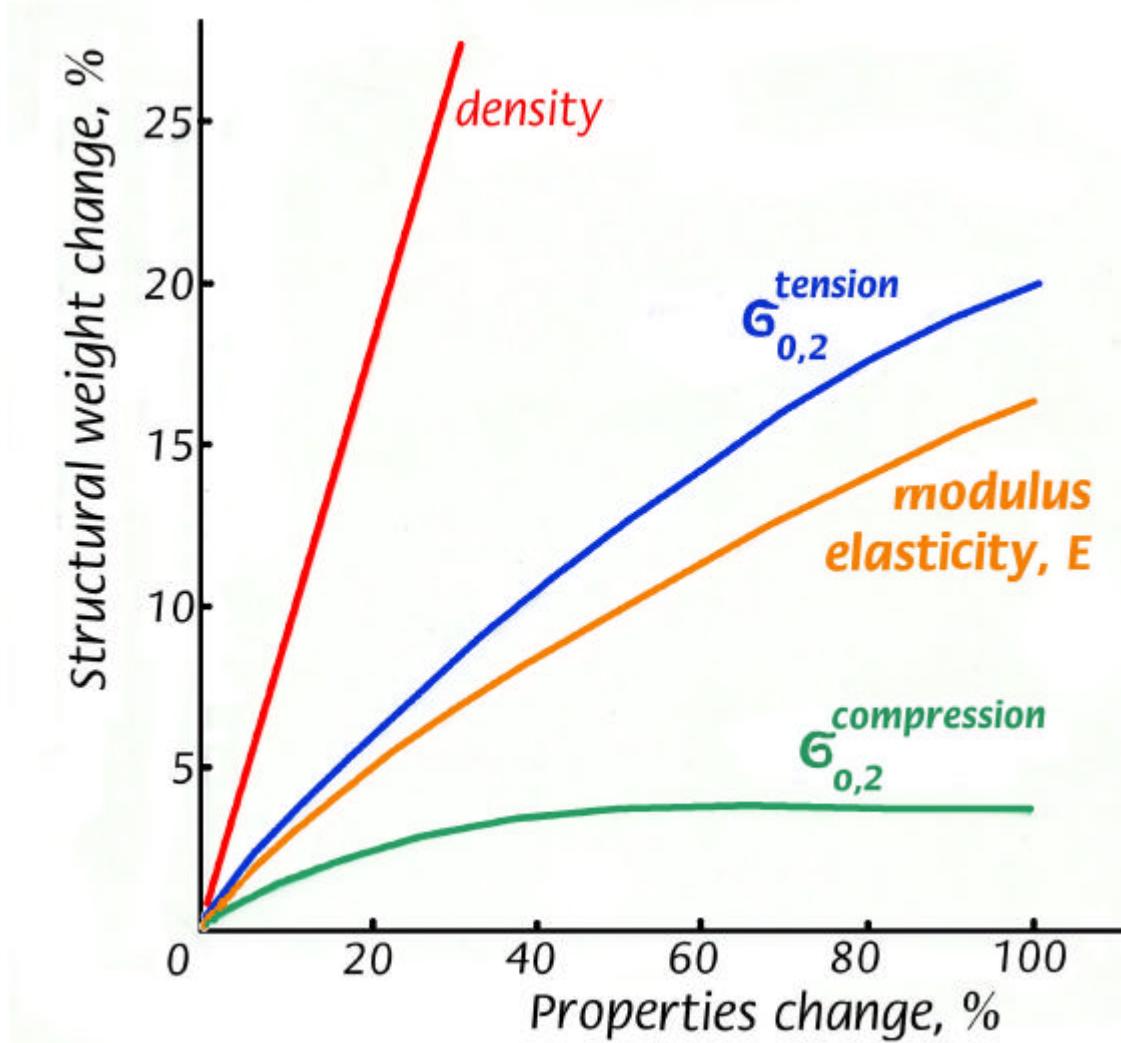
II – Metal matrix composites

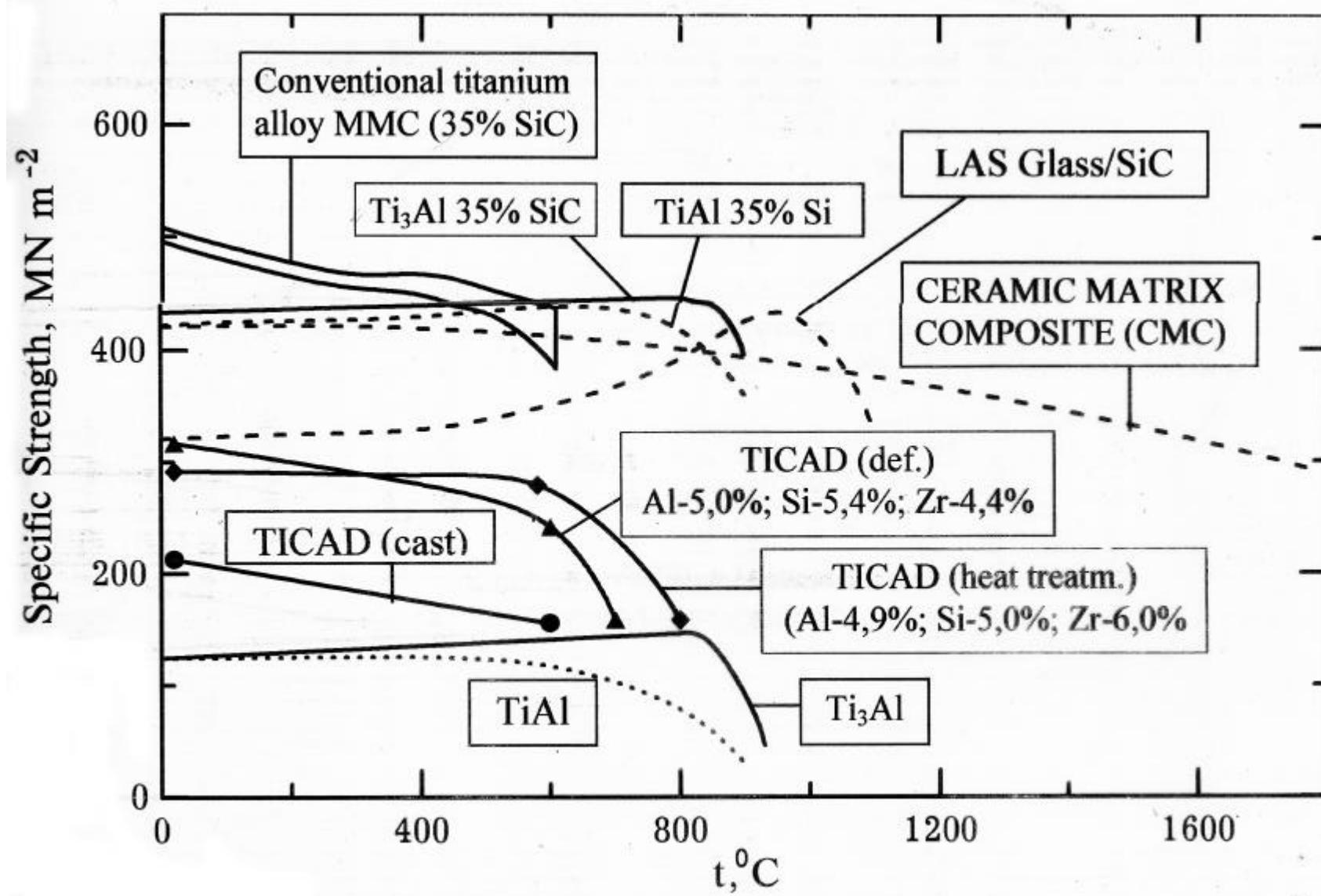
III – Ceramics

IV – Intremetallic
composites and intermetallic

V – Ceramic composites

VI – Carbon / carbon
composites





PART 1

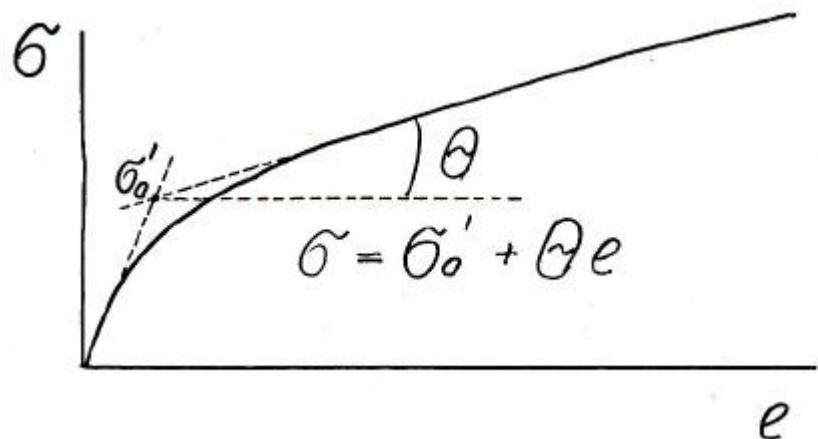
Nanostructured materials
produced via severe plastic
deformation and other
technologies



Unusual properties of nanomaterials

1. Reduced density (up to 10%)
2. Reduced modulus of elasticity (up to 10%) and Debye temperature (in the case iron 240K instead 476K)
3. Some severely deformed metals demonstrate good RT plasticity (Ti, Al, Cu)
4. Increased solubility of interstitial elements
5. (Carbon in Iron up to 1.2% instead 0.06% at RT)

DEFORMATION HARDENING



$$\mathbf{s} = \mathbf{s}'_s + \Theta e$$

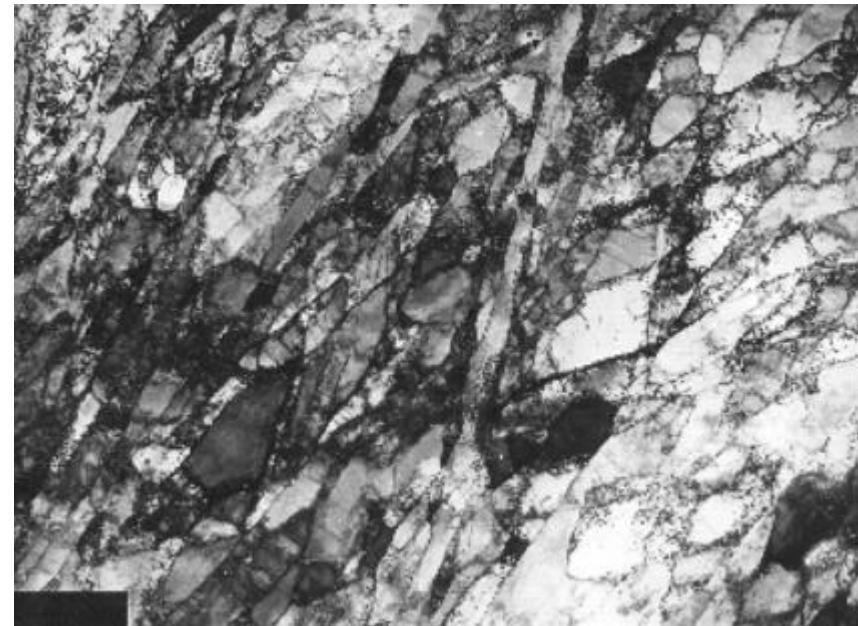
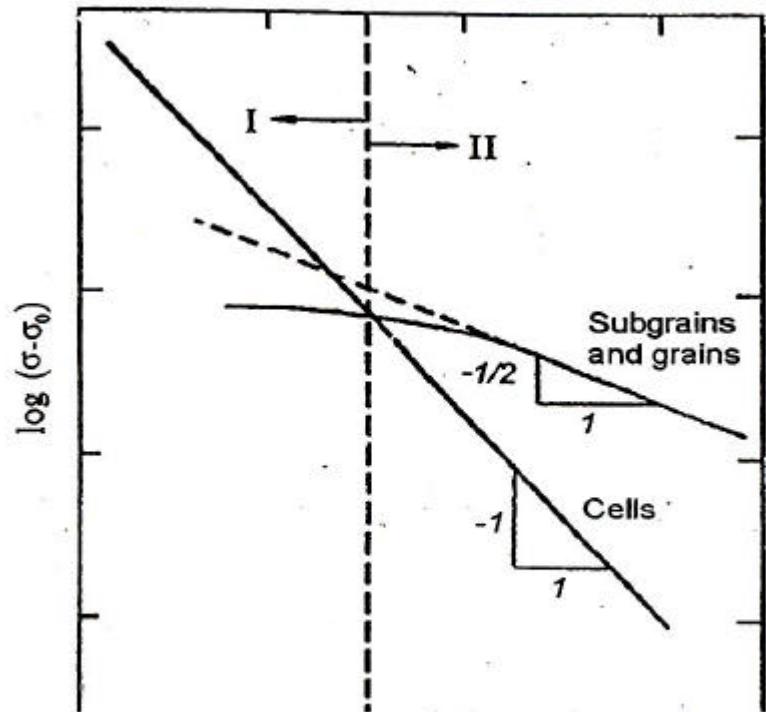
$$\mathbf{s} = \mathbf{s}_0 + k d^{-1}$$

$$d(e) = \frac{k}{\Delta s + \Theta e} = \frac{d_0}{1 + ae}$$

Material	$\sigma_{\text{theor}}, \text{ MPa}$	e_{ult}	$d_{\text{ult}}, \text{ m}$
Mo	11000	25	0.02
Fe	7130	40	0.02

MECHANISMS OF STRAIN HARDENING

(Thompson A.W.)



Efficiency of various mechanisms of hardening dependence of substructural elements (schematic diagram):
I – hardening cells;
II – hardening by grains prevails.

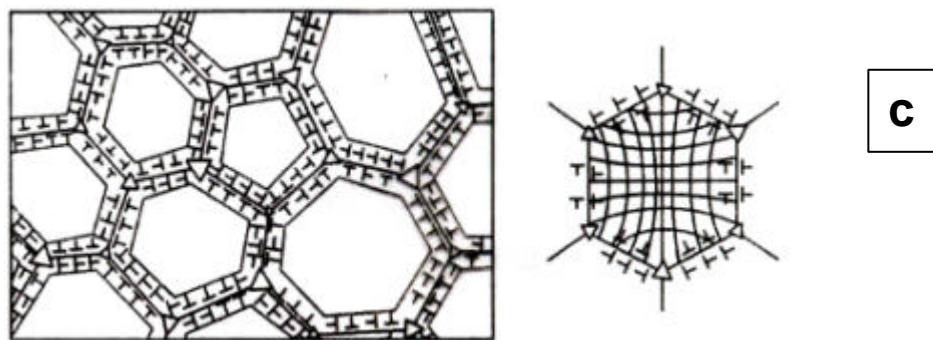
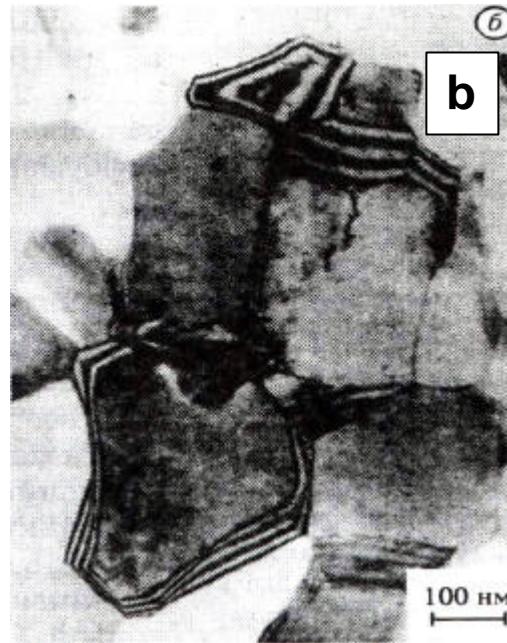
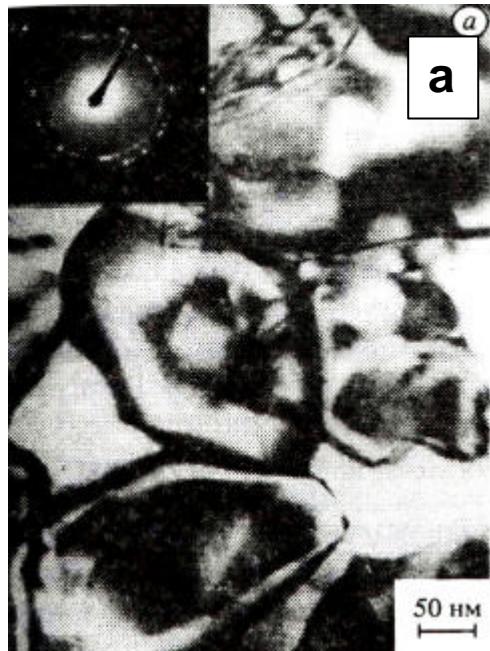
The critical sizes of structural elements (grains)

$$\Delta\sigma \sim d^{-0.5} \quad \textcircled{R} \quad \Delta\sigma \sim d^{-1}$$

$$0.4 \text{ } \mu\text{m} \leq d \leq 1 \text{ } \mu\text{m}$$

$$\sigma = \alpha G b / L \rightarrow \sigma_{\text{theor}}$$

$$d \leq 0.02 \text{ } \mu\text{m}$$



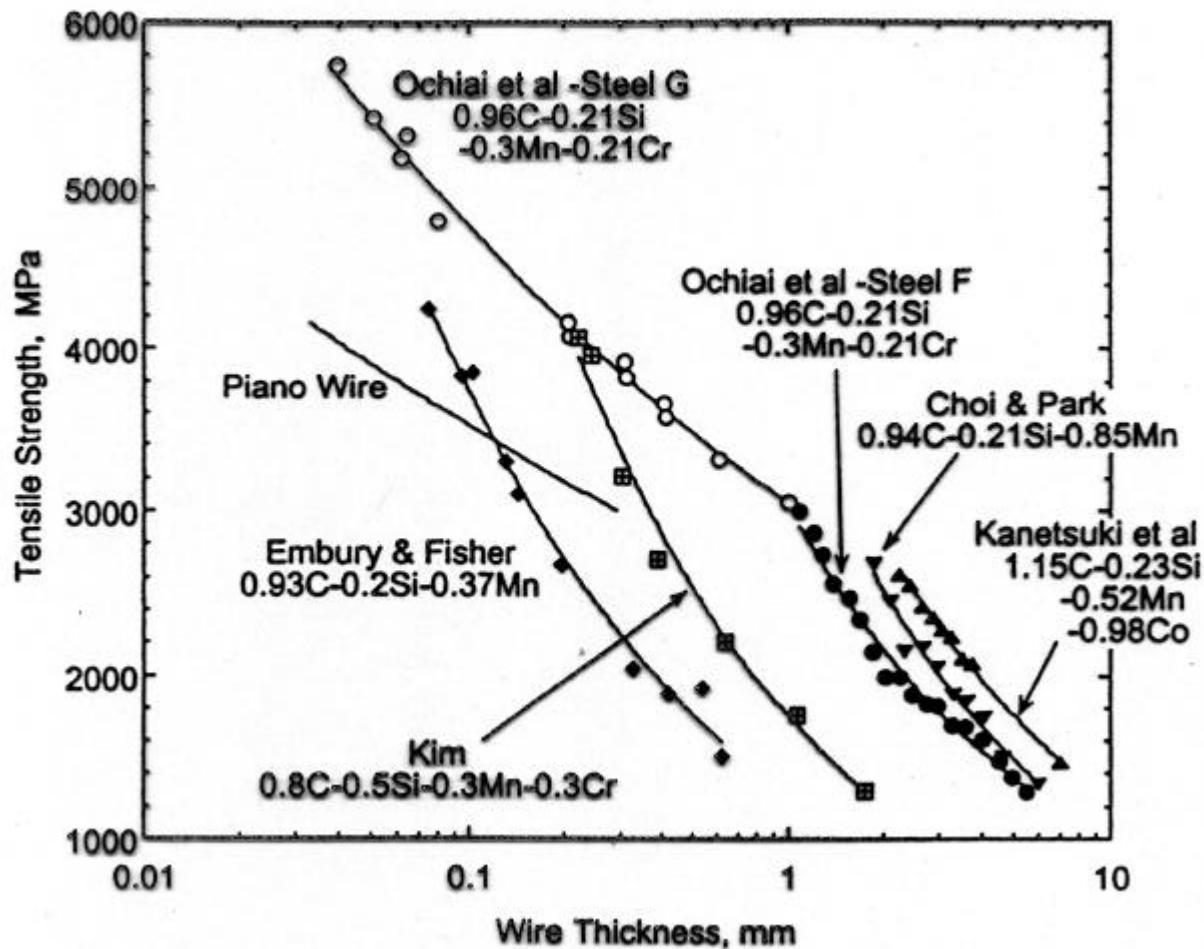
Grain boundary in the heavily deformed Al-4%Cu-0.5%Zr alloy:

- (a) after deformation at $e=7$ and $T=20$ °C;
- (b) after additional annealing at 160 °C for 1 h;
- (c) schematic illustration of the GB in nanostructured state

Valiev R.Z.

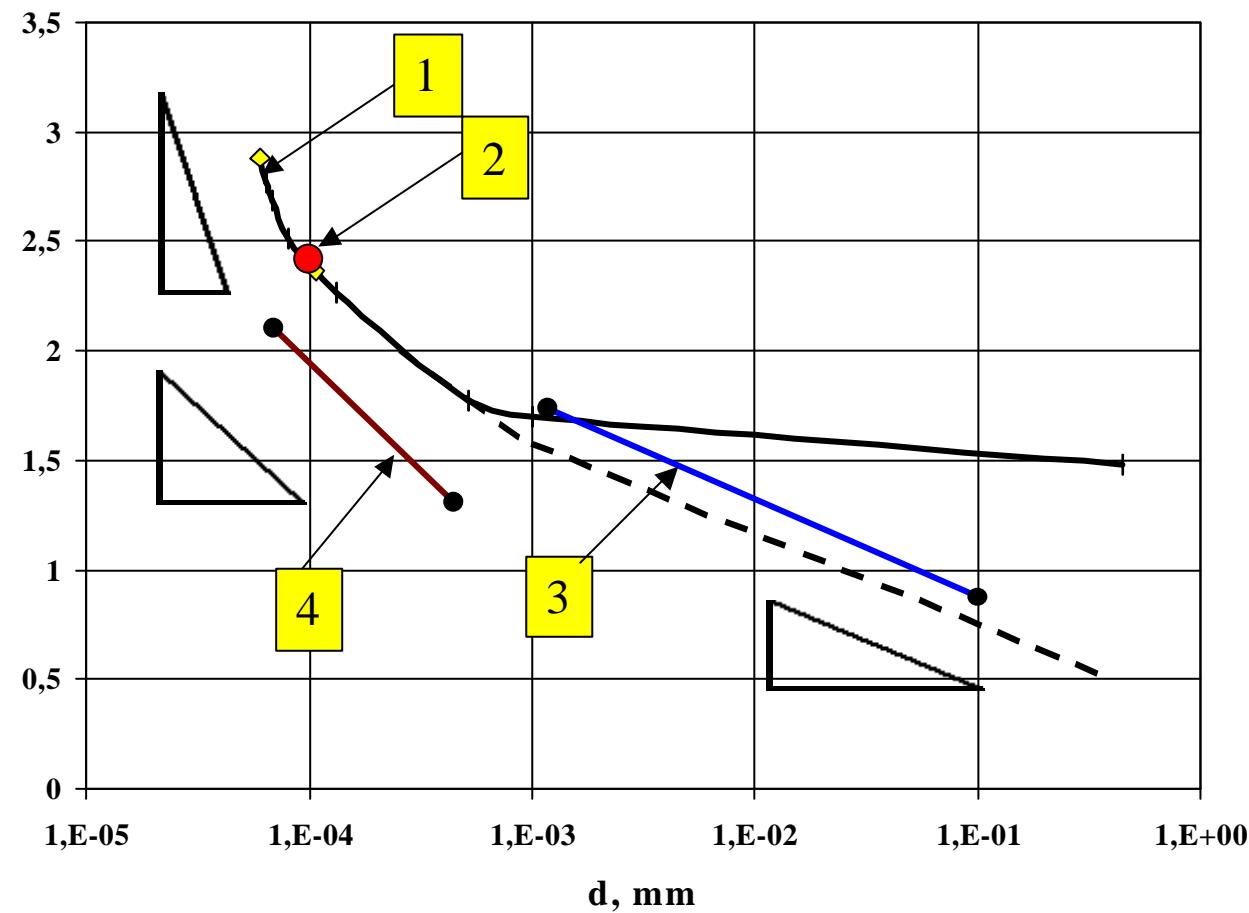
Grain boundary energy

- Low energy ($\gamma_b < 0.1 - 0.2 \gamma_0$) – amorphous/crystalline interface, special boundaries.
- Middle energy ($\gamma_b < 1/3 \gamma_0$) – ordered boundaries with random misorientation .
- High energy ($\gamma_b \rightarrow 2\gamma_0$) – non-equilibrium boundaries with disordered structure (boundaries produced during low temperature deformation).



Tensile strength as a function of wire diameter during wire drawing
for eutectoid and hypereutectoid steels

Chromium coatings produced by magnetron sputtering

 $\text{Lg}[\Delta\sigma]$ 

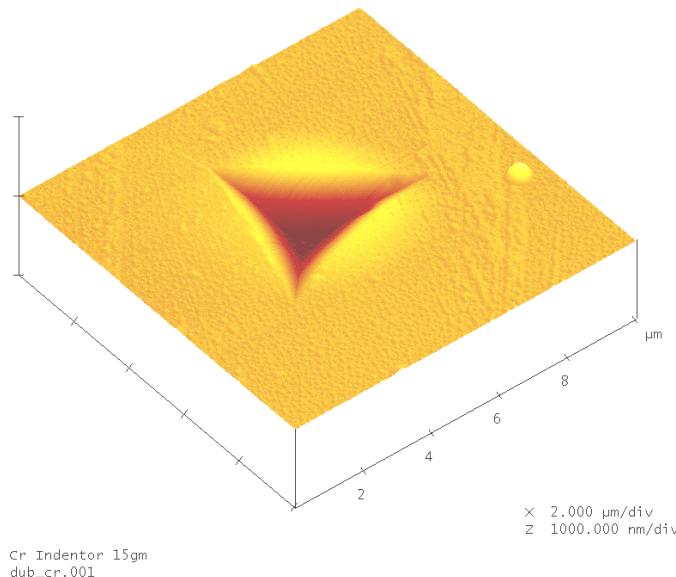
1 - magnetron sputtering of Cr coatings;
2 - ion-plasmic Cr coatings;
3 - (Fe-C);
4 - (Fe-0,49%Ti)



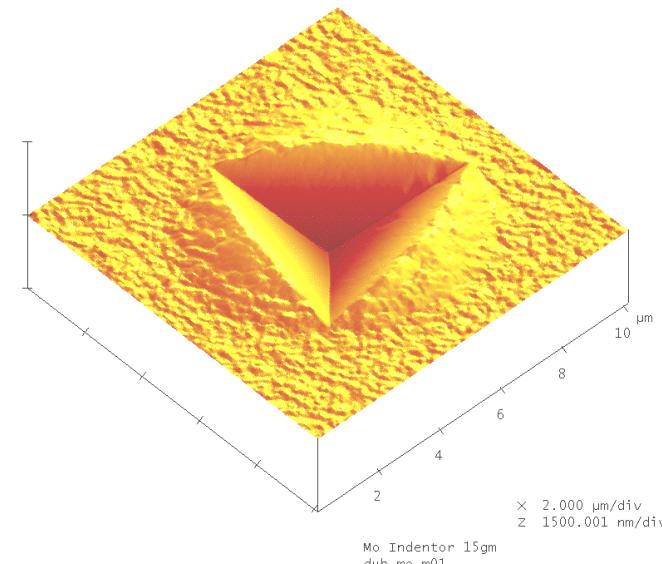
**Chromium coating
produced by magnetron
sputtering (t=400nm)**



AFM image of indentation made in the chromium and molybdenum produced by magnetron sputtering on silicon substrates

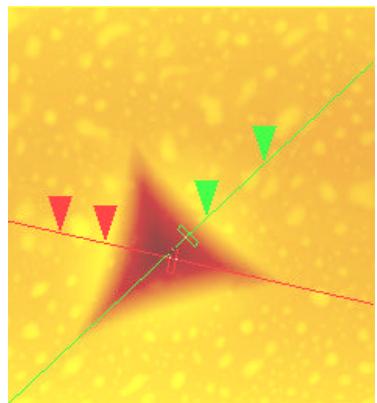


Cr

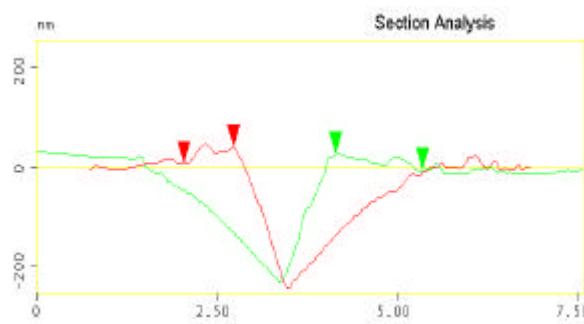


Mo

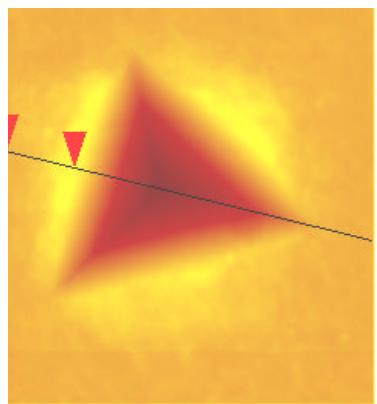




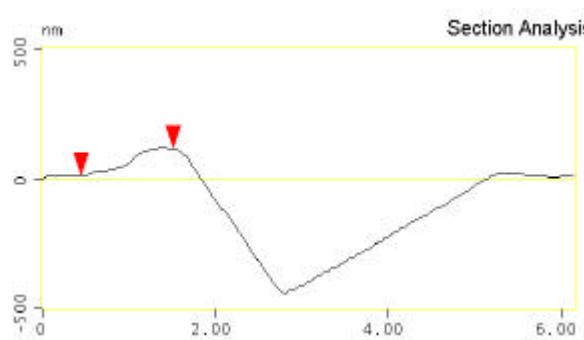
Indentor 5gm



Cr



Indentor 5gm



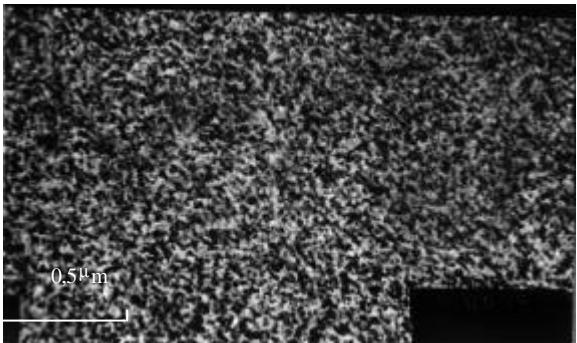
Mo

Cross-section of indentation in the chromium and molybdenum produced by magnetron sputtering on silicon substrates

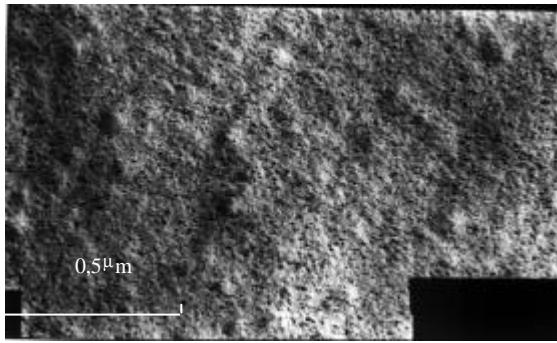
(AFM)

	Load, gm	Indentation depth, nm	Height of the pile-up, nm
Cr	5	235,69	33
Cr	15	409,3	98,7
Mo	5	377	104
Mo	15	661	198

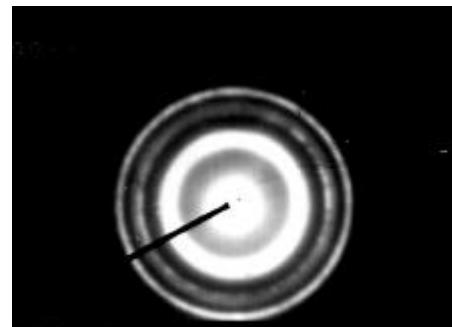
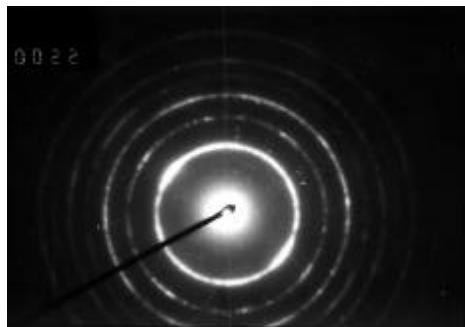
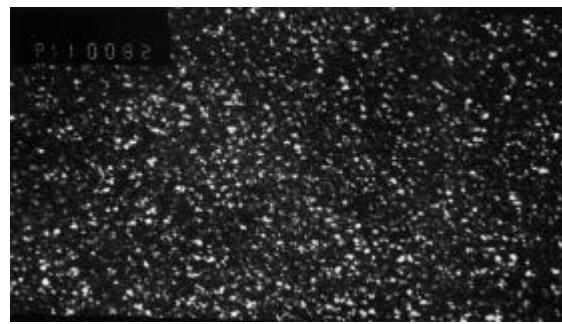
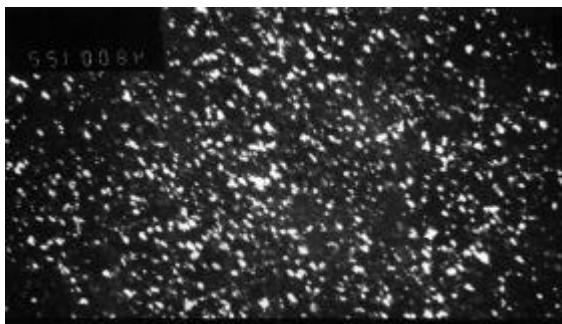
Cr



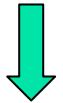
Mo



Chromium and
molybdenum
produced by
magnetron
sputtering



Boundary



$$M-M-M-M=M-M-M-M$$

$$M-M-M-M=M-M-M-M$$

$$M-M-M-M=M-M-M-M$$

$$M-M-M-M=M-M-M-M$$

$$M-M-M-M=M-M-M-M$$

$$M-M-M-M=M-M-M-M$$



$$M-M-M-M=M-M-M-M$$

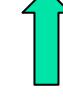
$$M-M-M-M=X-M-M-M$$

$$M-M-M-X=M-M-M-M$$

$$M-M-M-M=X-M-M-M$$

$$M-M-M-X=X-M-M-M$$

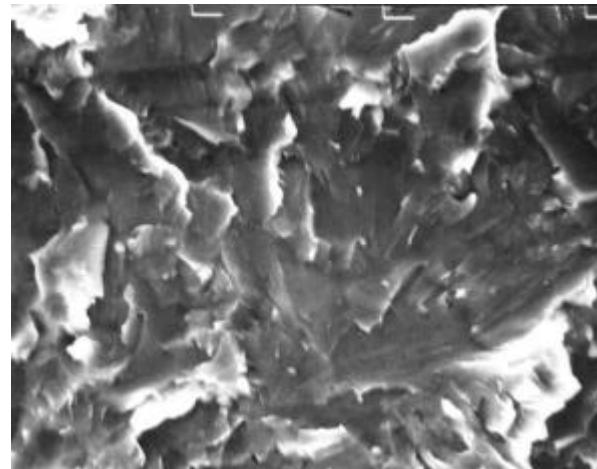
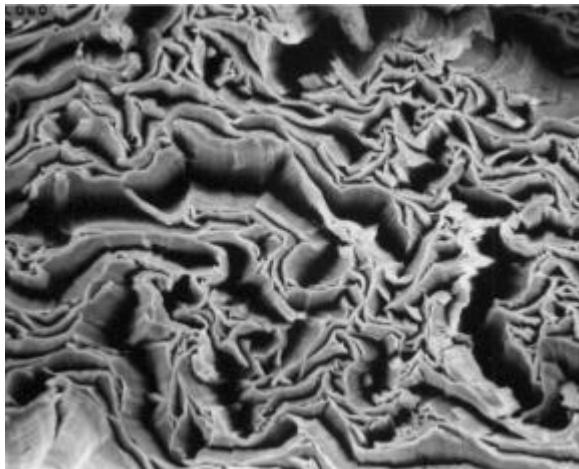
$$M-M-M-M=M-M-M-M$$



If $E_{xx} > E_{MM}$ and $E_{MX} > E_{MM}$ strength (hardness) increases.

If $E_{xx} (E_{MX}) < E_{MM}$ strength (hardness) decreases.

FRACTURE SURFACES OF HEAVILY DEFORMED Cr AND Mo



	-DH ₂₉₈		T _{melting} , K
	Kilojoules/mole	Kilocalorie/mole	
Cr	397.75	95.0	2173
Cr ₂ O ₃	1130.4	270.0	2538
Mo	659.42	157.5	2883
MoO ₂	548	131	2200

"Useful" impurities (additives) concept

Theoretical strength can be achieved at $d \approx 0.02 \mu\text{m}$. Practically, in one-component systems, the "negative" Hall-Petch (or strength saturation) has been observed in many investigations at the nanoscale level of grain sizes. The main reason for such phenomenon is the increase of the "bad" material volume in nanostructured materials with decreasing the grain size.

In multicomponent systems the possible **healing of the weak points** in the grain boundaries structure can occur and this can lead to the extremely high strength (hardness). Using the **segregation of the useful impurities** or alloying elements, it is possible to realize the healing of weak places in the grain boundaries and to obtain the essential increase of mechanical properties as a result.



PART 2

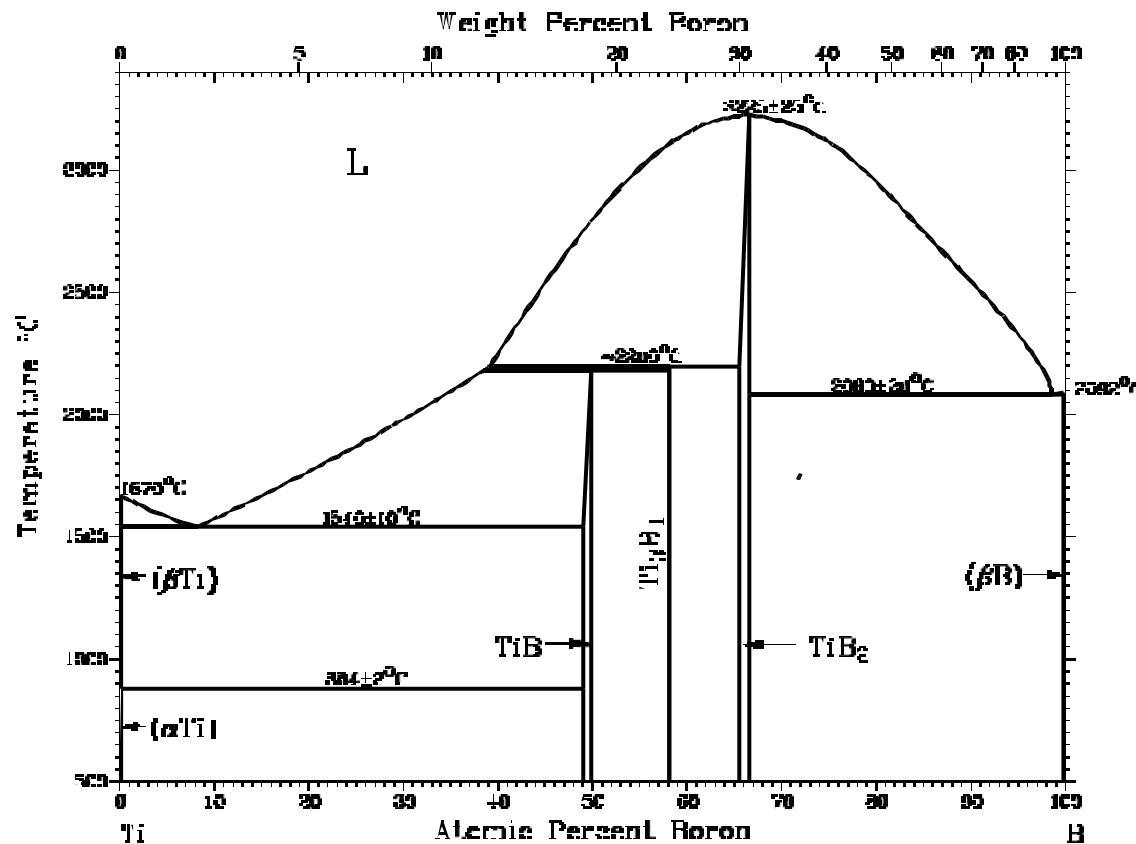
Advanced Ti – based materials



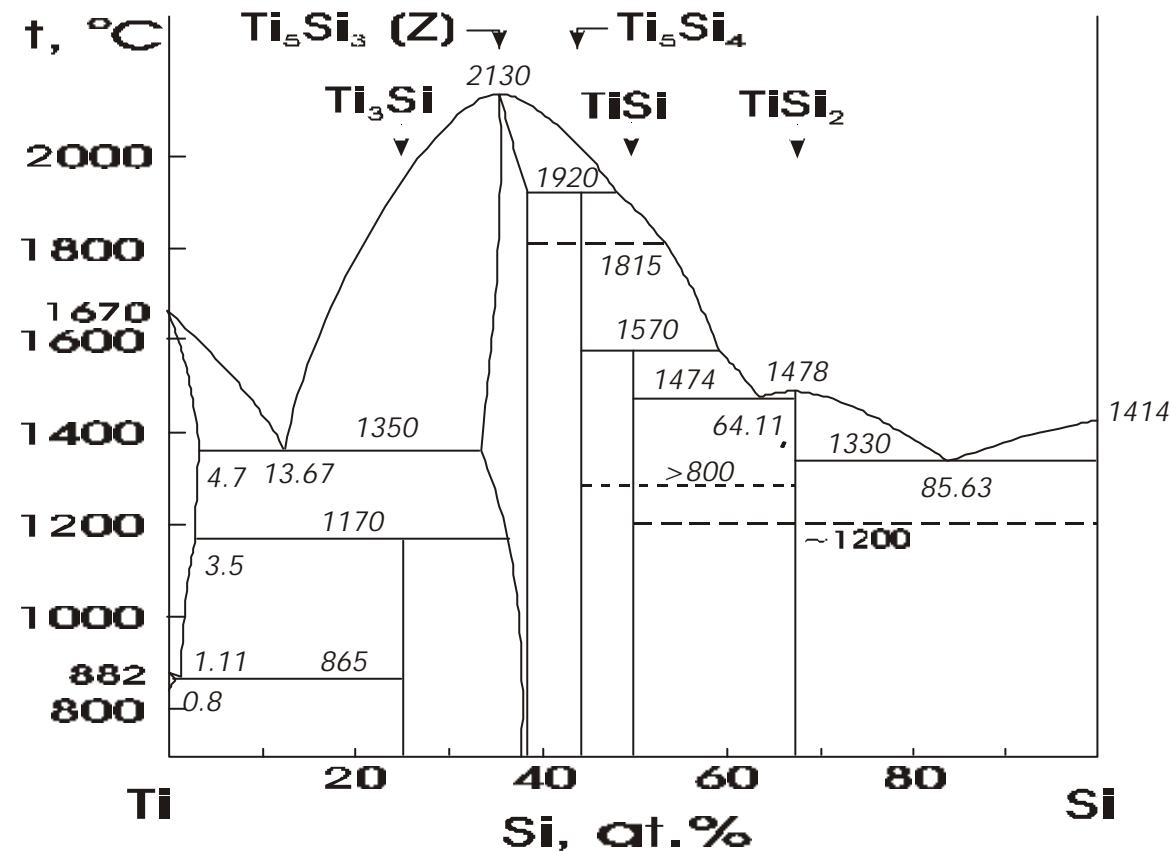
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Properties of Ti alloys and Discontinuously-Reinforced Ti (DRTi) materials

	Ti-6Al-4V	Ti-6Al-4V + 3% TiB	Ticompl. alloyed + 5% TiB	Ti-6Al-4V +10(20)% (TiB+TiC)	TENTATIVE GOAL	ACHIEVED Ti-9.0Al-2.2Zr-1.6Si deformed
Modulus (GPa)	110-115	125	132	141/168	$\geq 150\%$ of matrix = 170	~ 135 -140
YS (MPa)	840-1070	1007	1175	1406/ 1181	$\geq 140\%$ of matrix = 1400	-
UTS (MPa)	940-1180			1550/ 1215	$\geq 140\%$ of matrix = 1500	b 1180 a 1230
Strain (%)	7-20%	9.5	5.0	4.6/0.6	$\geq 5\%$	b 0.8 – 1.6 a 3.8 – 6.1
K _{IC} (MPa·√m)	44-66 ($\alpha+\beta$) 88-110 (β)	47			≥ 30	b 19.2 a 51.1
Max Oper. Temp	427°C (800°F)				$\geq 600^\circ\text{C}$ (~1100°F)	at 700 °C b 650 at 700 °C a 400

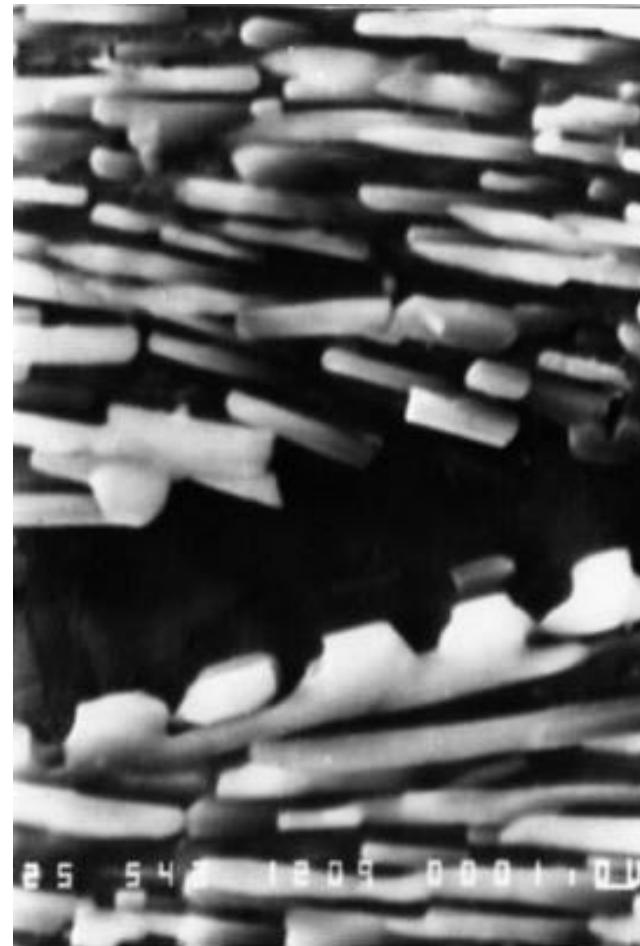
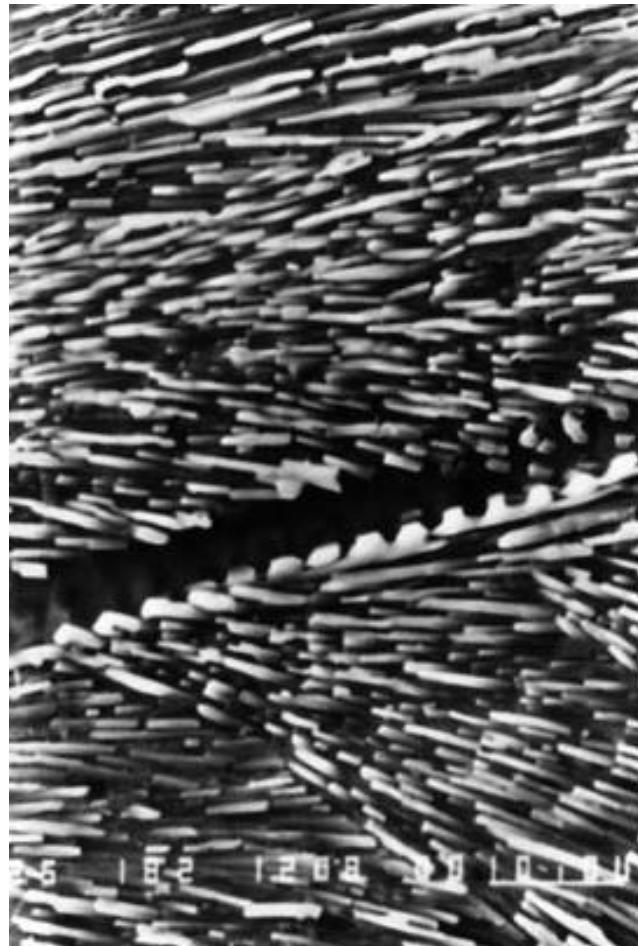


The Ti-B system from Massalski's handbook.

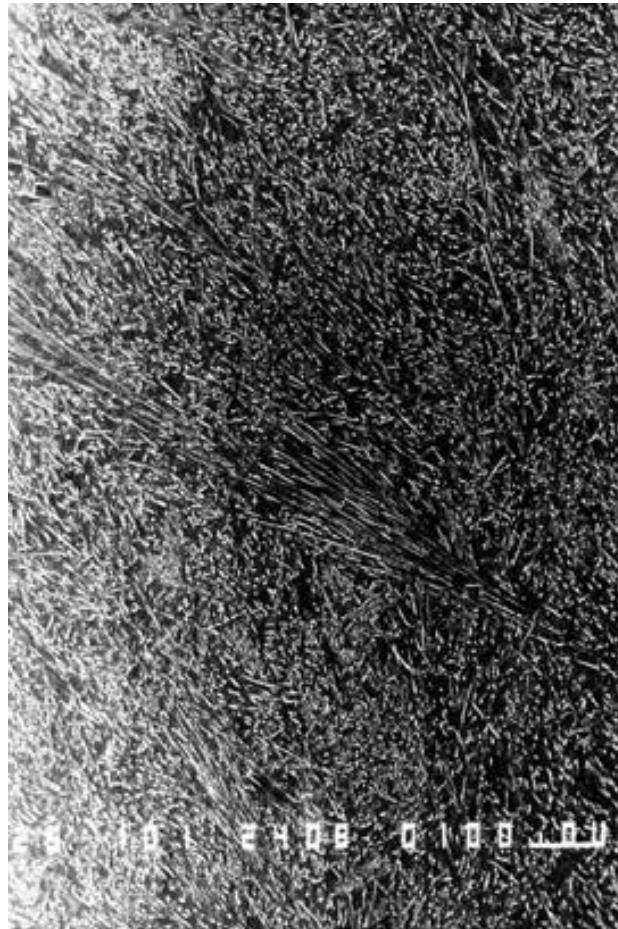


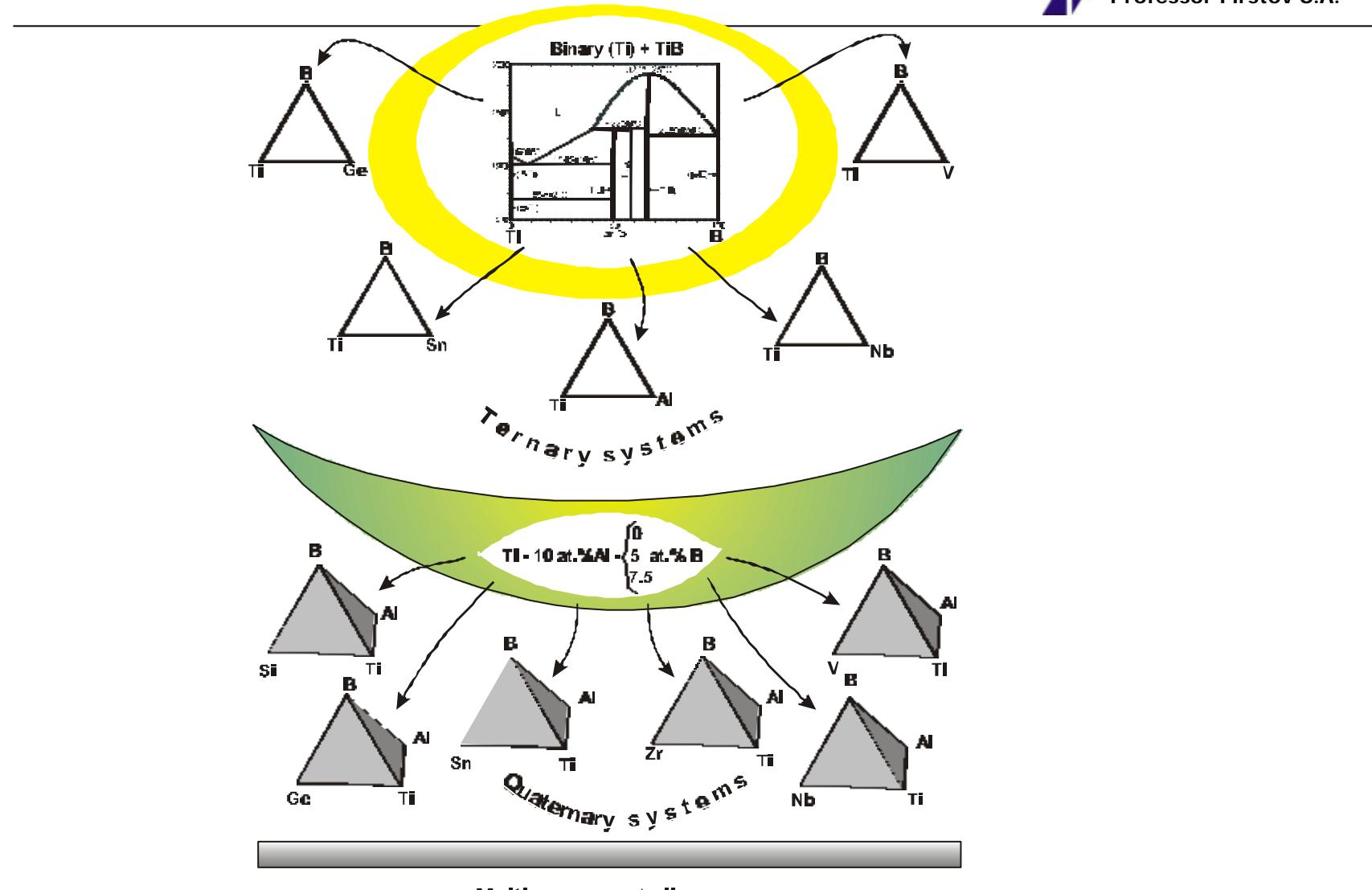
The Ti-Si system, Dr. Bulsnova's assessment.

Ti -8,5 Si (wt. %), DEEP ETCHING, SEM. UPERPROBE -733



Ti – 2.0 B (wt. %), STRUCTURE, SS

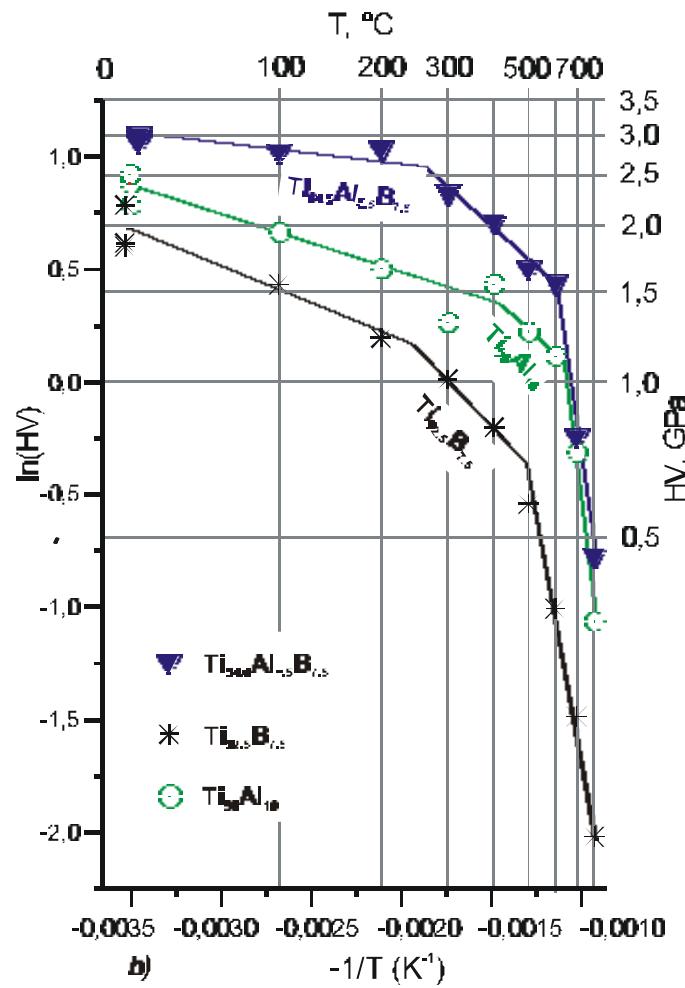
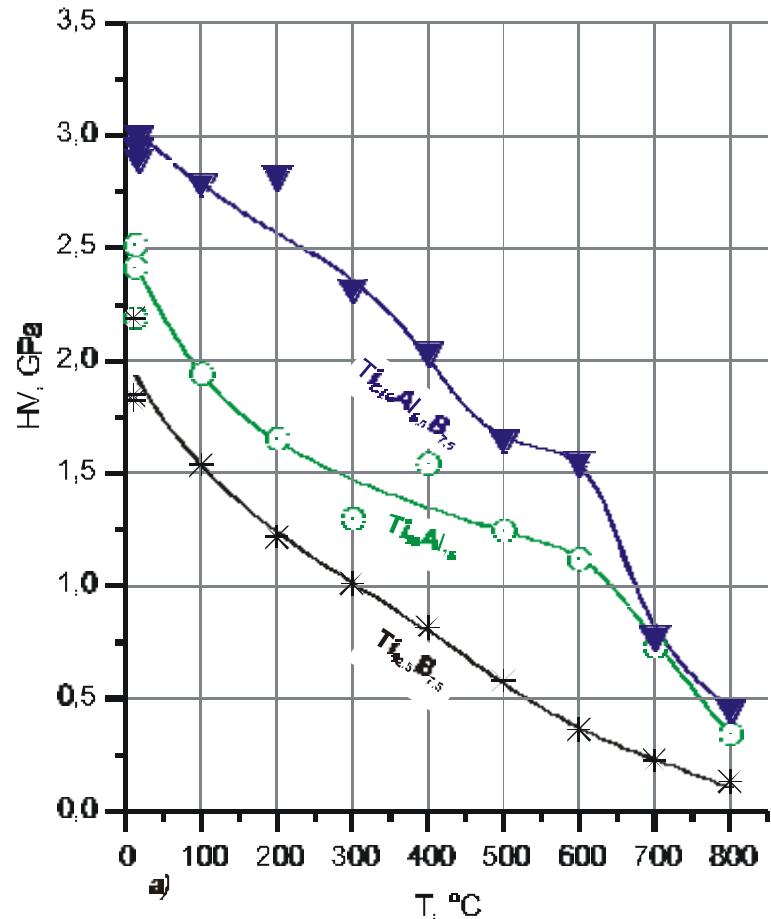




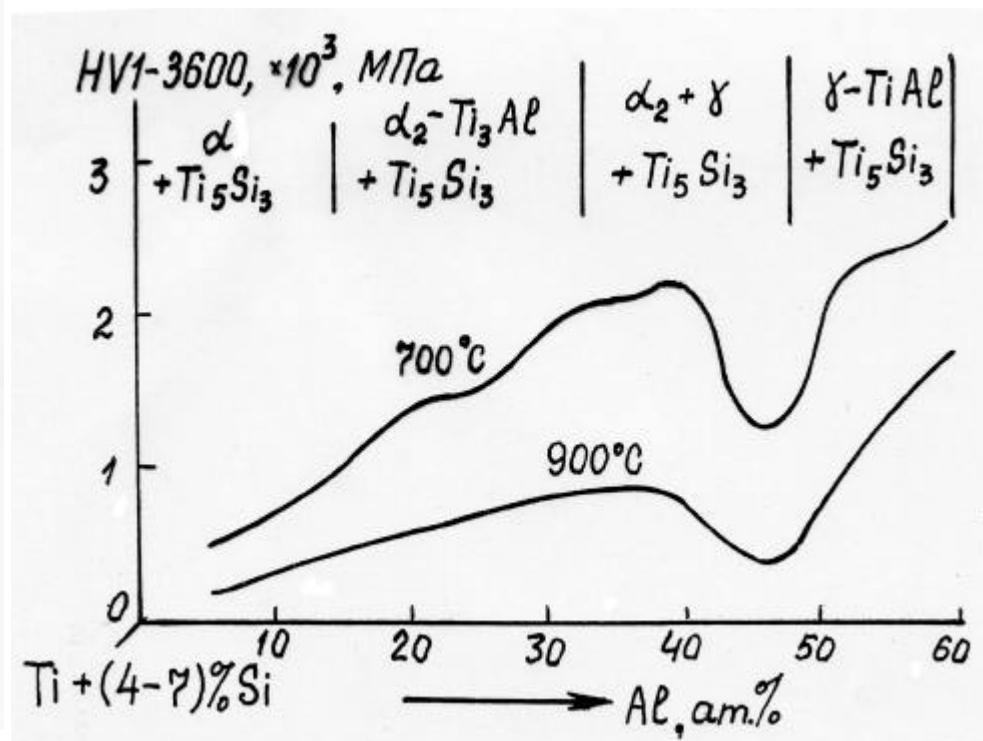
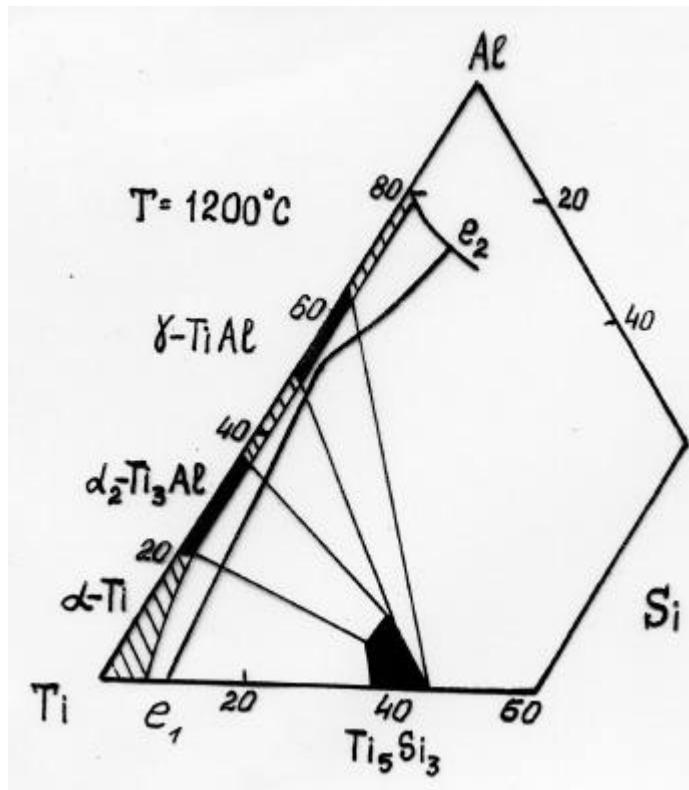
Multicomponent alloys:

$\text{Ti-Al-Ge-Sn-(0;5;7.5)B}$; $\text{Ti-Al-Ge-Sn-Zr-(0;5;7.5)B}$;
 $\text{Ti1100} + (\text{TiB})$; $\text{IM 1834} + (\text{TiB})$

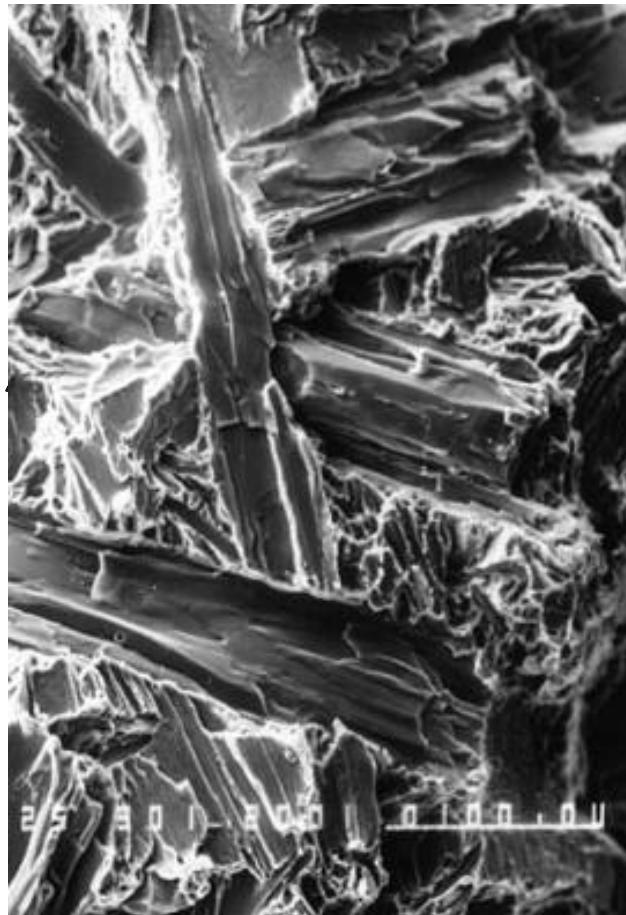
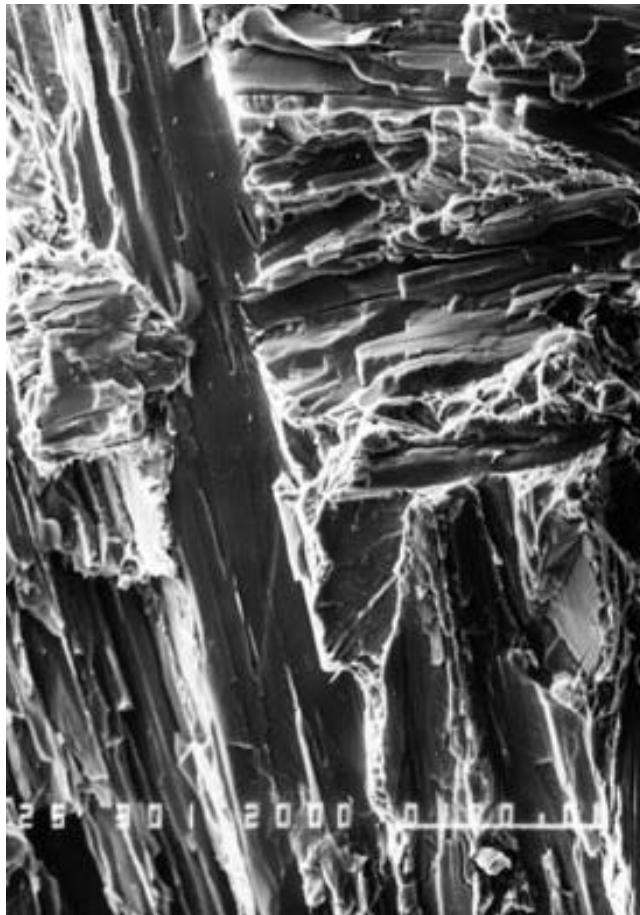
Strategy of research work on alloying of the binary $(\text{Ti}) + \text{TiB}$ eutectic alloy.



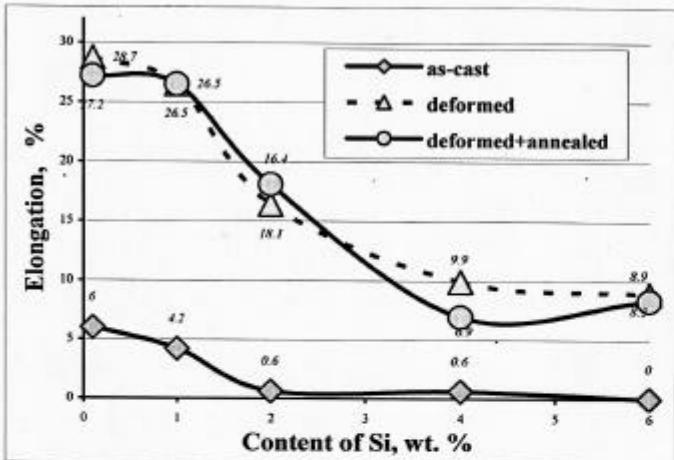
Contributions of alloying additives to the hardness of $\text{Ti}_3\text{Al}_5\text{B}_{15}$ alloy compared with the appropriate binaries, HV vs T (a) and $\lg(\text{HV})$ vs $-(1/T)$ (b).



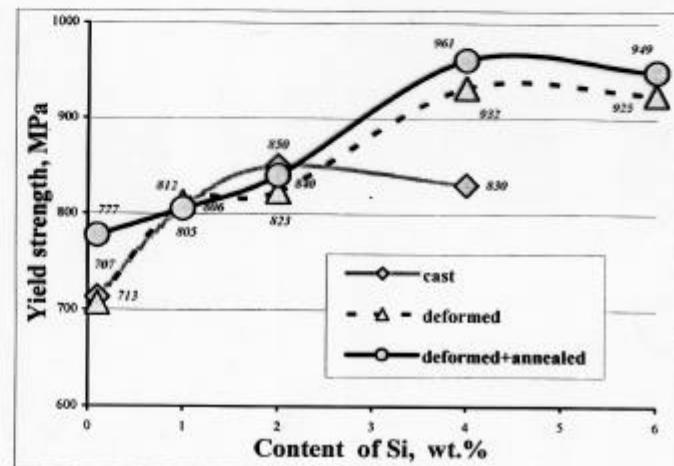
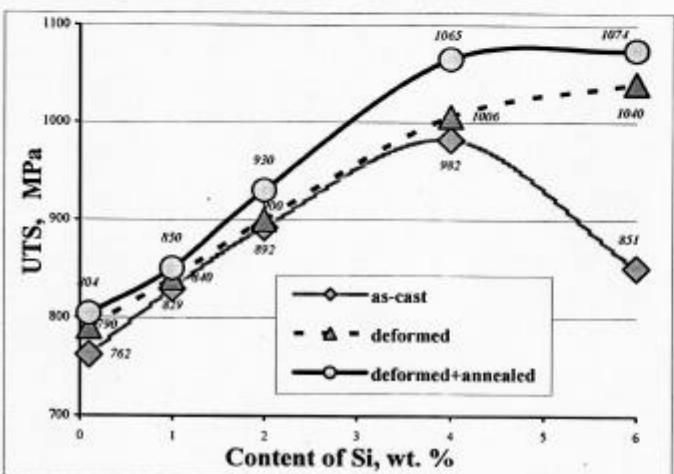
FRACTURE MICROMECHANISMS OF AS-CAST Ti – 3.5 B, iod, 20°C



Binary Ti – Si system



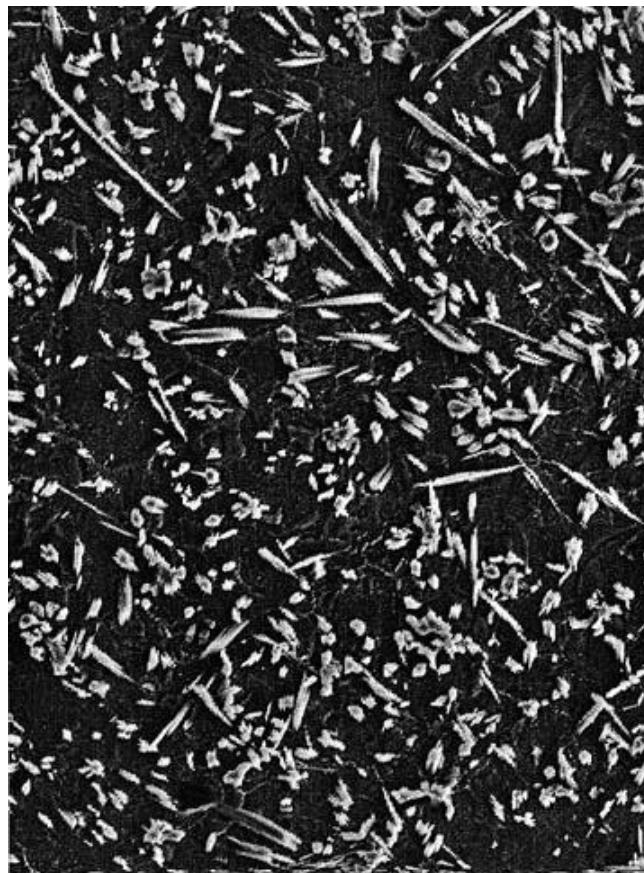
Ultimate tensile strength (UTS), yield strength and plasticity (elongation, δ) of commercial titanium alloy BT1-0 vs. silicon content in it for as-cast, deformed (forged for 90 %) and forged + annealed at 800 °C for 2 hours states.



Properties of selected alloys after forging, $\varepsilon > 60\%$

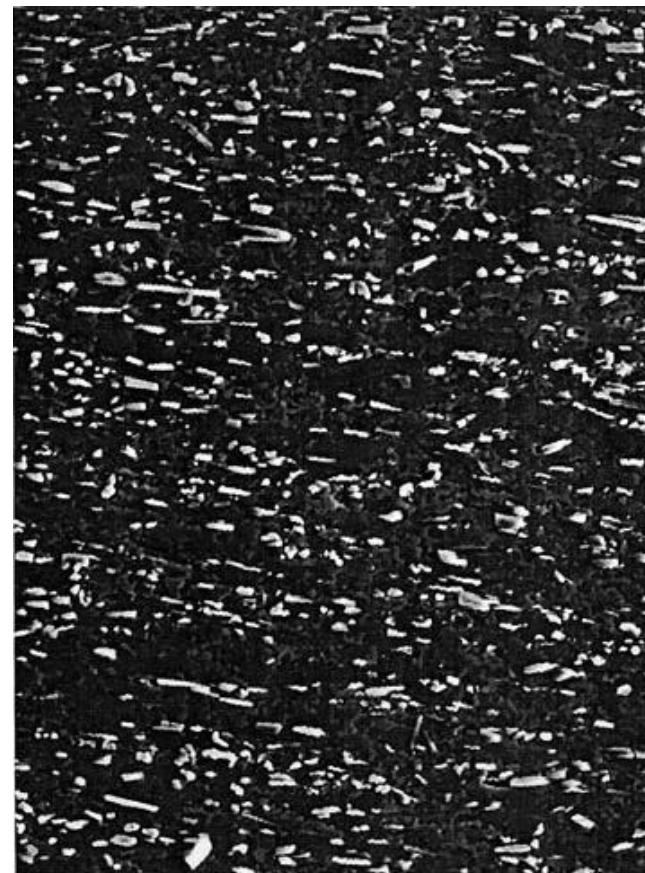
Alloy	RT strength, UTS, MPa	RT fracture toughness K_{Ic} , MPa m ^{1/2}	RT yield strength, $s_{0.2}$ MPa;	RT elongation, $\delta\%$;	RT fracture micro- mechanism	Elasticity modulus, GPa
Ti-6.3Al-5Zr-1.8Si LM-863	1220		1120	5.4	void coalescence	
	in process					
Ti-6.6Al-3.5Zr-1.3Si-1.1B LM-908	1530		1469	1.4	void coalescence	158
	in process					
Ti-9.0Al-2.2Zr-1.6Si LM-905	1302			1.83	void coalescence	~140
	^b 1180 ^a 1230	^b 19.2 ^a 51.1		^b 0.8 – 1.6 ^a 3.8 – 6.1		
Ti-5.5Al-1.9B LM-903	1184		1140	6.24	void coalescence	152
	in process					

Structure of as-cast (a) and as-forged (b) Ti – Al – Zr – Si - B



a

X 400 SEI



b

X 400 SEI



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Ternary Ti-B system

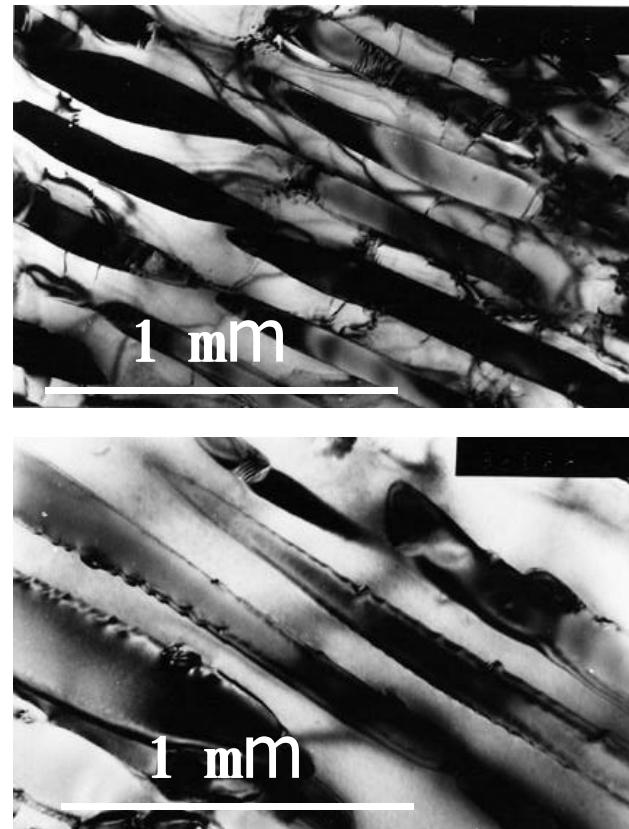
Tensile yield strength ($\sigma_{0.2}$), ultimate tensile strength (UTS), plasticity (elongation, δ) and elasticity modulus (E) of complex alloyed Ti-B alloys, deformed and annealed (800°C, 2 hours), at room temperature. Produced with arc (AM) and electron beam melting (EBM) of BTI-O alloy.

Chemical composition	Melting	As-cast			Forged			
		UTS, MPa	$\sigma_{0.2}$, MPa	δ , %	UTS, MPa	$\sigma_{0.2}$, MPa	δ , %	E, GPa
Ti-3Al-1.2B (2B-57)	AM	1020	1000	1,2	1033	972	7.2	137-138
Ti-5.5Al -1.9B (LM-903) annealed 800 °C	EBM	-	-	-	1184	1140	6.24	151-152

Ti – Al – Si – B

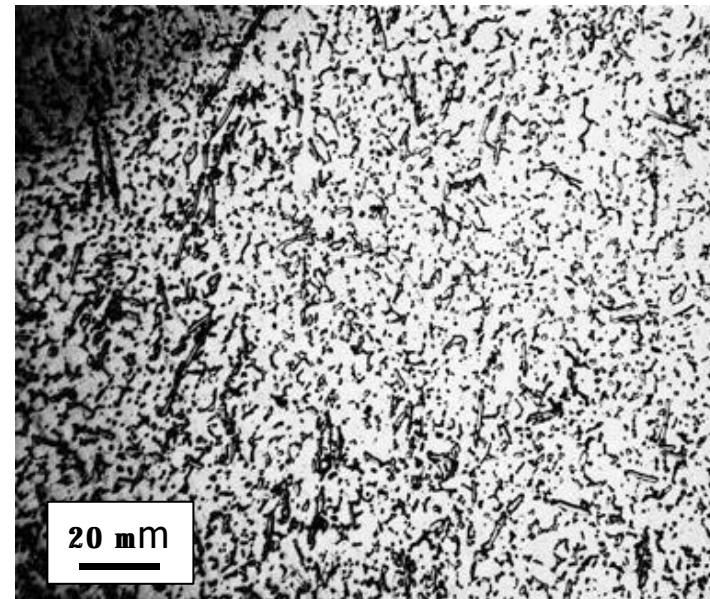
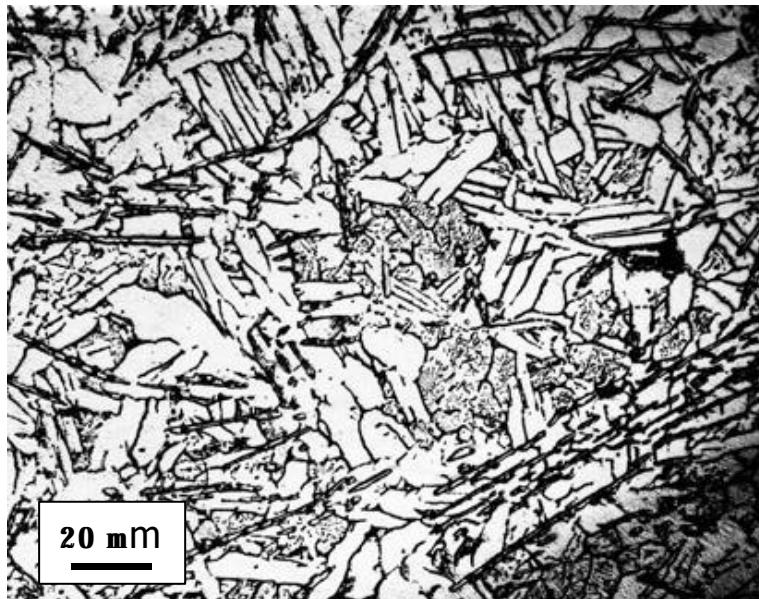


Ti – Si – B



Structure of as-cast and as-rolled alloys

Ti – 4Al – 4Zr – 1Si – 2B



CONCLUSIONS

The following directions of R&D in the field of elaboration of materials with high specific strength are actual:

1. Further elaboration of different methods producing of nanostructured materials including gradient nanostructured materials
2. Grain boundary engineering of nanostructured materials including thermo-chemical treatment based on concept of "useful" additives
3. Clarifying of the mechanisms of plasticity in nanostructures. Achievement of a good combination of different mechanical properties (σ , δ , ψ , K_{Ic} , fatigue properties, heat resistance etc.)
4. Phase equilibria investigations of multicomponent systems as base for producing of advanced materials strengthened by quasicrystals, intermetallics, creation in situ composites, nanocomposites, nanolaminates, amorphous structures etc.
5. Further development lightweight materials including porous materials with different volume and morphology of pores



As to Ti-based materials:

1. Ti-Si-X systems alloys are attractive for creation of heat resistant materials
2. Ti-B-X systems alloys are promising for achievement of high specific stiffness
3. Further investigations of Ti-B-Si-X alloys.
Amorphisation, icosahedral phase production, search of new strengthening phases
4. Methods of obtaining of alloys with high boron content
5. Ti-Si-X systems alloys are a good matrix for producing MMM's